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INTERNAL REPORT

CORRECTIONS TO THE THIRD VIRIAL COEFFICIENT FOR THE MODIFIED BUCKINGHAM EXPONENTIAL-6 POTENTIAL FOR HELIUM

BY

John C. Edwards

BRANCH Fundamental Research

PROJECT NO. 7017

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CONTENTS

Page

Abstract 4

Introduction 5

Acknowledgment 7

Nonadditive attractive interaction 7

Nonadditive repulsive interaction 8

Expression for the third virial coefficient 13

Computations of C^*_{add} 18

Computations of $\Delta C^*_{rep}/\sqrt{\epsilon^*}$ 18

Computations of $\Delta C^*_{att}/\alpha^*$ 19

Comparison of C^*_{add}, ΔC^*_{rep}, and ΔC^*_{att} 19

Distribution functions for ΔC^*, ΔC^*_{rep}, and ΔC^*_{att} 21

Conclusions 22

References 23

ILLUSTRATIONS

Fig.

1. Ratio of first order nonadditive repulsion energy to total pair repulsion energy for an equilateral triangle configuration 12

2. Distribution functions for ΔC^*, ΔC^*_{rep}, and ΔC^*_{att} at $T^* = 10$ 21

3. Distribution functions for ΔC^*, ΔC^*_{rep}, and ΔC^*_{att} at $T^* = 100$ 21

TABLES

Page

1. Computer results for $\varphi(r)$, $\Delta \varphi_{att}$, and $\Delta \varphi_{rep}$ for equilateral triangle configuration for 1.0 Å $< r <$ 5.0 $<$ 11

2. Computer results for C^*_{add}, $\Delta C^*_{rep}/\sqrt{\epsilon^*}$, and $\Delta C^*_{att}/\alpha^*$ for five reduced temperatures 17

3. ΔC^*_{att} for $\alpha = .201$ Å^3 and $\alpha = .210$ Å^3, ΔC^*_{rep} for $\epsilon/K = 9.16°$ K, and ΔC^* 20

4. Percent ratio of $|\Delta C|$ to $|C_{add}|$ 20

CORRECTIONS TO THE THIRD VIRIAL COEFFICIENT FOR THE MODIFIED BUCKINGHAM EXPONENTIAL-6 POTENTIAL FOR HELIUM

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ABSTRACT

The objective of this work is to determine the contribution of nonadditive interatomic interactions (attractive and repulsive) to the classical third virial coefficient for an assumed modified Buckingham Exponential-6 pair potential for helium. Methods of statistical physics were used to determine corrections to the third virial coefficient. In these calculations the results of Kihara (4)[2] for the nonadditive three body attractive interaction between three spherically symmetric atoms, and Sherwood, De Rocco, and Mason's (10) asymptotic approximation to Jansen's (3) expression for nonadditive three body repulsive interactions based upon an assumed Gaussian charge distribution were employed. Computer calculations were executed for several reduced temperatures.

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[1] Project leader, Helium Research Center, Bureau of Mines, Amarillo, Tex.

[2] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

These calculations were carried out using programs HA 2983, HA 2860, and HA 3068, which were prepared by the Automatic Data Processing Branch of the Helium Activity. The results, based on improved numerical calculations, confirm the conclusion of Sherwood and coworkers (10) and Sherwood and Prausnitz (11) that the nonadditive effects tend to cancel each other, and hence the total correction is not strongly dependent upon the pair potential selected.

INTRODUCTION

As part of Physics Project 7017 at the Helium Research Center, consideration is being given to a determination of the correction to the third virial coefficient due to nonadditive interatomic interactions for helium. The work of other investigators was followed. The total interaction among three atoms was written as the sum of the pair interactions, and nonadditive corrections to the attractive and repulsive parts of the pair interaction. The pair interaction selected was the Modified Buckingham Exponential-6 potential (hereafter referred to as MBE6). This selection was based on its functional resemblance to the theoretical potentials for helium of Slater and Kirkwood (12) and Margenau (5). The short range repulsive part of a typical pair potential is based upon first order perturbation theory with exchange, whereas the long range attractive part of the pair interaction is based upon second order perturbation theory using wave functions that do not satisfy the Pauli principle. The nonadditive repulsive correction considered here comes from first order perturbation theory with exchange applied

to three atoms, where each atom is assumed to be surrounded by an "effective" electron represented by a Gaussian charge distribution, the model of Jansen (3). The nonadditive attractive interaction considered comes from third order perturbation theory applied to the dipole-dipole interaction among three atoms, that neglects overlap and exchange. This model was developed by Axilrod and Teller (1) and Kihara (4). These results, and Sherwood's approximation to Jansen's result, were used to calculate the linear corrections to the third virial coefficient, as well as the additive part of the third virial coefficient, for several reduced temperatures.

Corrections to the third virial for the Lennard-Jones (12, 6) potential have been calculated by Sherwood and coworkers (10). Sherwood and Prausnitz (11) have computed the correction to the third virial due to nonadditive attractive interactions for the MBE6 potential for $\gamma \geq 15$[3]. This work extends their results by considering both attractive and repulsive corrections to the third virial for an assumed two body MBE6 potential that has γ set equal to 12.4 on the basis of Mason and Rice's (6) analysis of helium data.

Although the cumulative correction to the third virial coefficient is small, it is important to have as much information as possible for helium on the relationship between the interatomic potential and the third virial coefficient in order to obtain the best equation of

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[3] For definition of γ see representation of MBE6 potential on page 10.

state, and a description of the relationship of the microscopic interactions to the observed macroscopic thermodynamic properties.

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NONADDITIVE ATTRACTIVE INTERACTION

Second order interactions between spherical neutral atoms are additive if the Pauli principle is not taken into account in the wave functions (5, 8). The result is the usual additive, $-\mu$ (atomic separation)$^{-6}$, term. The next consideration is third order perturbation theory applied to dipole-dipole interactions among three atoms, and yields the nonadditive result in the absence of overlap and exchange

$$\Delta \varphi_{att} = \nu \left(r_{12} r_{13} r_{23} \right)^{-3} \left[1 + 3 \cos \theta_1 \cos \theta_2 \cos \theta_3 \right] \quad (4) \quad (1)$$

where θ_i is the angle formed by the interatomic distances r_{ij} and r_{ik}. The quantity ν is related to the static polarizability and the constant μ in the second order attractive term $-\mu\, r^{-6}$, where r is the interatomic separation, by the relationship

$$\nu = \frac{3}{4} \alpha \mu . \qquad (2)$$

Assuming the ratio $\Delta \varphi_{att} / \sum_{i(<j)=1}^{3} \varphi_{att} \left(r_{ij} \right)$ to be independent

of the explicit functional form chosen for $\varphi_{att}\left(r_{ij}\right)$, it is possible to express $\Delta\varphi_{att}$ as

$$\Delta\varphi_{att} = -\frac{3}{4}\,\alpha\,\frac{\sum \varphi_{att}\left(r_{ij}\right)}{\sum r_{ij}^{-6}}\left(r_{12}r_{13}r_{23}\right)^{-3} \times \left[1 + 3\cos\theta_1\cos\theta_2\cos\theta_3\right]. \qquad \underline{(11)} \tag{3}$$

The quantity $\Delta\varphi_{att}$ is positive if all θ_i are less than 117°, and consequently weakens the attractive forces. If one of the θ_i is greater than 126°, then $\Delta\varphi_{att}$ is negative. However, the latter case is less probable.

It should be noted that Graben, Present, and McCulloch (2) considered the second-order single-overlap exchange contribution. However, as pointed out by Sherwood and coworkers (10), it is inconsistent to consider such a correction without including the corresponding term in the pair potential.

NONADDITIVE REPULSIVE INTERACTION

As mentioned earlier, the repulsive part of the pair potential is based upon first order perturbation theory with exchange. Extending the analysis to three helium atoms, Rosen (9), used hydrogenic wave functions and considered interatomic and intra-atomic exchange of electrons in a first order calculation, to determine the nonadditive repulsive interaction. The results are in the form of a number of cumbersome quadratures. In order to have a simple analytic form for $\Delta\varphi_{rep}$, Sherwood and coworkers (10) approximated the Gaussian model

of Jansen (3) for near-equilateral triangle configuration of atoms with fairly large interatomic separation. It is in this spirit that the calculations of this report were pursued.

Jansen (3) considers each atom to be surrounded by a Gaussian charge distribution, namely,

$$\rho(r) = \left(\beta/\sqrt{\pi}\right)^3 \exp\left(-\beta^2 r^2\right) \tag{4}$$

which is equivalent to an "effective" electron on that atom. The distance from the center of the given atom is denoted by r, and β is a constant dependent upon the species under consideration. Single interatomic exchange is accounted for between two and three atoms. Jansen used the wave function associated with the above charge distribution, and constructed the properly antisymmetrized wave function for three atoms, to calculate the nonadditive correction to the repulsive interaction. Sherwood's approximation (see above) yields, for three atoms,

$$\Delta \varphi_{rep} = -2\, e^2 \Delta_{12}\Delta_{13}\Delta_{23} \left[r^{-1}_{1(23)} + r^{-1}_{2(13)} + r^{-1}_{3(12)} - r^{-1}_{12} - r^{-1}_{13} - r^{-1}_{23} \right], \tag{5-a}$$

and for a pair of atoms the approximation reads

$$\varphi_{rep} = e^2 \frac{\Delta^2}{r}, \tag{5-b}$$

where

$\Delta_{ij} = \exp\left(-\beta^2 r^2_{ij}/4\right)$; r_{ij} is the distance between atoms i and j,

$r_{i(jk)}$ is the distance from atom i to the midpoint of the line joining atoms j and k, and e is the electronic charge expressed in esu.

Equations 5-a and 5-b imply

$$\Delta \varphi_{rep} = -\frac{2}{e}\left[\varphi_{rep}\left(r_{12}\right)\varphi_{rep}\left(r_{13}\right)\varphi_{rep}\left(r_{23}\right)\right]^{1/2}\left(r_{12}r_{13}r_{23}\right)^{1/2}$$

$$\times\left[r_{1(23)}^{-1} + r_{2(13)}^{-1} + r_{3(12)}^{-1} - r_{12}^{-1} - r_{13}^{-1} - r_{23}^{-1}\right] \qquad (6)$$

Equations 3 and 6 are expressed in terms of an assumed two body potential. The explicit form of the MBE6 potential used in this report is

$$\varphi(r) = \begin{cases} \infty & r < m \\ \dfrac{\epsilon}{1 - \dfrac{6}{\gamma}}\left[\dfrac{6}{\gamma}\exp\left[\gamma\left(1 - \dfrac{r}{r_m}\right)\right] - \left(\dfrac{r}{r_m}\right)^{-6}\right] & r > m \end{cases}$$

where ϵ is the depth of the potential well at its minimum r_m, m locates the position of the spurious maximum, and γ influences the steepness of the repulsive part of the potential.

In table 1 a listing of $\Delta\varphi_{rep}$ and $\Delta\varphi_{att}$ for an equilateral triangle configuration and the MBE6 pair potential φ is given for $1\ \text{Å} < r < 5\ \text{Å}$. In the MBE6 potential the force constants determined by Mason and Rice (6) from an analysis of second virial coefficients and viscosity data for helium were used. These are

$\gamma = 12.4$

$\epsilon/k = 9.16°\ \text{K}$

$r_m = 3.135\ \text{Å}$.

For the atomic polarizability the value $\alpha = .201\ \text{Å}^3$ reported by Kihara (4) for helium was used.

TABLE 1. - Computer results for $\varphi(r)$, $\Delta\varphi_{att}$, and $\Delta\varphi_{rep}$ for equilateral triangle configuration for $1.0\ \text{Å} < r < 5.0\ \text{Å}$

r, cm	$\Delta\varphi_{att}$, ergs	$\Delta\varphi_{rep}$, ergs	$\varphi(r)$, ergs
1.0000000000E-08	4.8213811910E-13	-2.5015424812E-12	3.1869364899E-12
1.1000000000E-08	2.0447362804E-13	-1.4495616329E-12	2.3990061237E-12
1.2000000000E-08	9.3441597551E-14	-8.3649514852E-13	1.7203737635E-12
1.3000000000E-08	4.5465429545E-14	-4.8103529178E-13	1.2009687471E-12
1.4000000000E-08	2.3335609475E-14	-2.7580475053E-13	8.2418732067E-13
1.5000000000E-08	1.2541518924E-14	-1.5773054884E-13	5.5873886962E-13
1.6000000000E-08	7.0160330376E-15	-9.0004171142E-14	3.7506377186E-13
1.7000000000E-08	4.0656611227E-15	-5.1257753315E-14	2.4952308099E-13
1.8000000000E-08	2.4306303889E-15	-2.9140957600E-14	1.6450576883E-13
1.9000000000E-08	1.4941323218E-15	-1.6541573821E-14	1.0737041265E-13
2.0000000000E-08	9.4167601388E-16	-9.3766452454E-15	6.9240594459E-14
2.1000000000E-08	6.0701275473E-16	-5.3085339029E-15	4.3971794933E-14
2.2000000000E-08	3.9936255476E-16	-3.0019865966E-15	2.7352611761E-14
2.3000000000E-08	2.6768309506E-16	-1.6958748006E-15	1.6517882923E-14
2.4000000000E-08	1.8250312021E-16	-9.5712343570E-16	9.5298497378E-15
2.5000000000E-08	1.2638961509E-16	-5.3971538020E-16	5.0846209104E-15
2.6000000000E-08	8.8799667080E-17	-3.0409825246E-16	2.3089338536E-15
2.7000000000E-08	6.3226274407E-17	-1.7121491438E-16	6.2064057220E-16
2.8000000000E-08	4.5577362256E-17	-9.6332135330E-17	-3.6644972013E-16
2.9000000000E-08	3.3234525930E-17	-5.4165609059E-17	-9.0714697787E-16
3.0000000000E-08	2.4495154148E-17	-3.0438112635E-17	-1.1685202121E-15
3.1000000000E-08	1.8235439076E-17	-1.7095050963E-17	-1.2592803542E-15
3.2000000000E-08	1.3703189526E-17	-9.5961494402E-18	-1.2494962167E-15
3.3000000000E-08	1.0388336536E-17	-5.3840792510E-18	-1.1837795386E-15
3.4000000000E-08	7.9407443804E-18	-3.0194399227E-18	-1.0900718910E-15
3.5000000000E-08	6.1172900103E-18	-1.6925964166E-18	-9.8547856490E-16
3.6000000000E-08	4.7473249785E-18	-9.4842524582E-19	-8.8012552442E-16
3.7000000000E-08	3.7098466046E-18	-5.3123316212E-19	-7.7969685391E-16
3.8000000000E-08	2.9182271910E-18	-2.9744630254E-19	-6.8709432924E-16
3.9000000000E-08	2.3098831248E-18	-1.6648746492E-19	-6.0351502025E-16
4.0000000000E-08	1.8392109646E-18	-9.3156184654E-20	-5.2914466758E-16
4.1000000000E-08	1.4727083826E-18	-5.2108201787E-20	-4.6359860954E-16
4.2000000000E-08	1.1855717865E-18	-2.9138773229E-20	-4.0619780389E-16
4.3000000000E-08	9.5930204236E-19	-1.6289708271E-20	-3.5613790255E-16
4.4000000000E-08	7.8000498977E-19	-9.1041179914E-21	-3.1258959448E-16
4.5000000000E-08	6.3717517269E-19	-5.0868655237E-21	-2.7475529322E-16
4.6000000000E-08	5.2281854505E-19	-2.8415504837E-21	-2.4189852865E-16
4.7000000000E-08	4.3081493239E-19	-1.5869302906E-21	-2.1335663808E-16
4.8000000000E-08	3.5645140667E-19	-8.8605769194E-22	-1.8854355650E-16
4.9000000000E-08	2.9607841627E-19	-4.9462023779E-22	-1.6694701807E-16
5.0000000000E-08	2.4685471698E-19	-2.7605225844E-22	-1.4812286043E-16

It is seen from table 1 that the individual corrections to the three body interaction fall off rapidly with increasing interatomic separation, and that $\Delta \varphi_{rep}$ dominates over $\Delta \varphi_{att}$ up to $r \cong 3$ Å, at which point $\Delta \varphi_{att}$ becomes the dominant term. The result is that, except for a small region past the zero of the potential, the total correction has a quenching influence on the two body potential.

For the equilateral triangle case, Rosen's (9) quantum mechanical calculation for helium yields as an asymptotic approximation for $r/r_m \geq 0.3$

$$\frac{\Delta \varphi_{rep}}{\sum \varphi_{rep}} = -1.15 \exp\left(-5.86516 \frac{r}{r_m}\right). \tag{8}$$

This quantity is compared in figure 1 with $\frac{\Delta \varphi_{rep}}{\sum \varphi_{rep}}$ for Sherwood's

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Figure 1. - Ratio of First Order Nonadditive Repulsion Energy to Total Pair Repulsion Energy for an Equilateral Triangle Configuration.

---

approximation to Jansen's result for equilateral triangle configuration, namely

$$\frac{\Delta \varphi_{rep}}{\sum \varphi_{rep}} = -2\left(\frac{2}{\sqrt{3}} - 1\right) \exp\left[-\left(\frac{1}{2} \beta \frac{r}{r_m}\right)^2\right], \tag{9}$$

and with equation 6 without the Gaussian dependence, that is

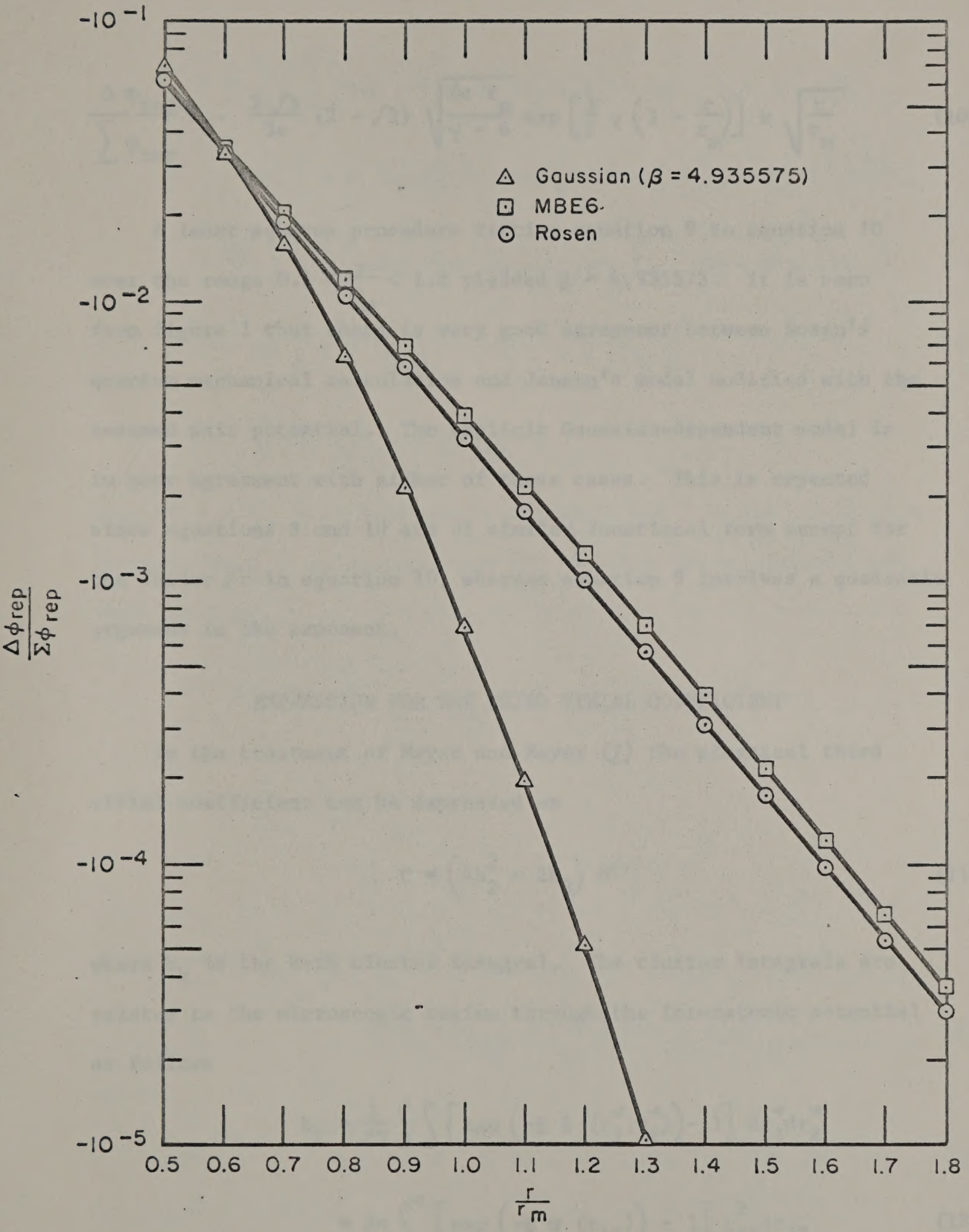

FIGURE 1. – Ratio of First Order Nonadditive Repulsion Energy to Total Pair Repulsion Energy for an Equilateral Triangle Configuration.

$$\frac{\Delta \varphi_{rep}}{\sum \varphi_{rep}} = - \frac{2\sqrt{3}}{3e} (2 - \sqrt{3}) \sqrt{\frac{6\epsilon \; r_m}{\gamma - 6}} \exp\left[\frac{1}{2} \gamma \left(1 - \frac{r}{r_m}\right)\right] x \sqrt{\frac{r}{r_m}} \tag{10}$$

A least squares procedure fitting equation 9 to equation 10 over the range $0.5 < \frac{r}{r_m} < 1.8$ yielded $\beta = 4.935575$. It is seen from figure 1 that there is very good agreement between Rosen's quantum mechanical calculation and Jansen's model modified with the assumed pair potential. The explicit Gaussian-dependent model is in poor agreement with either of these cases. This is expected since equations 8 and 10 are of similar functional form except for the factor $\sqrt{r}$ in equation 10, whereas equation 9 involves a quadratic argument in the exponent.

EXPRESSION FOR THE THIRD VIRIAL COEFFICIENT

In the treatment of Mayer and Mayer (7) the classical third virial coefficient can be expressed as

$$C = \left(4b_2^2 - 2b_3\right) N^2 \tag{11}$$

where b_k is the k-th cluster integral. The cluster integrals are related to the microscopic regime through the interatomic potential as follows

$$\begin{aligned} b_2 &= \frac{1}{2V} \int\int \left[\exp\left(-\beta \; \Phi \; (\vec{r_1},\vec{r_2})\right) - 1\right] d\vec{r_1} d\vec{r_2} \\ &= 2\pi \int_0^\infty \left[\exp\left(-\beta \; \varphi \; (r_{12})\right) - 1\right] r_{12}^2 dr_{12} \end{aligned} \tag{12-a}$$

$$b_3 = \frac{1}{6V} \int\int\int \Big[\exp\left(-\beta\, \Phi\, (\vec{r_1},\vec{r_2},\vec{r_3})\right) - \exp\left(-\beta\, \Phi\, (\vec{r_1},\vec{r_2})\right)$$

$$- \exp\left(-\beta\, \Phi\, (\vec{r_2},\vec{r_3})\right) - \exp\left(-\beta\, \Phi\, (\vec{r_1},\vec{r_3})\right) + 2\Big]\, d\vec{r_1}\, d\vec{r_2}\, d\vec{r_3}$$

$$= \frac{4\pi^2}{3} \int\int\int \Big[\exp\left(-\beta\, \varphi\, (r_{12},r_{23},r_{31})\right) - \exp\left(-\beta\, \varphi\, (r_{12})\right)$$

$$- \exp\left(-\beta\, \varphi\, (r_{23})\right) - \exp\left(-\beta\, \varphi\, (r_{13})\right)$$

$$+ 2\Big]\, r_{12} r_{23} r_{31}\; dr_{12}\, dr_{23}\, dr_{31} \quad . \qquad (12\text{-b})$$

where $\beta = 1/kT$, k is Boltzmann's constant, and T is the temperature. Decomposing $\varphi\, (r_{12},r_{23},r_{31})$ into its additive and its nonadditive contributions,

$$\varphi(r_{12},r_{23},r_{31}) = \sum_{i<j=1}^{3} \varphi\, (r_{ij}) + \Delta\, \varphi_{rep} + \Delta\, \varphi_{att} \qquad (13)$$

and introducing the quantity

$$f_{ij} = \exp\left(-\, \varphi\, (r_{ij})/kT\right) - 1 \qquad (14)$$

it is possible to express C(T) as

$$C(T) = C_{add}\, (T) + \Delta C(T) \qquad \underline{(10)} \qquad (15)$$

where

$$C_{add}(T) = -\, \frac{8\pi^2 N^2}{3} \int\int\int f_{12} f_{23} f_{13} r_{12} r_{13} r_{23} dr_{12} dr_{23} dr_{13} \qquad (16)$$

$$\Delta C(T) = - \frac{8\pi^2 N^2}{3} \int\int\int \exp\left(- \frac{\sum \varphi\ (r_{ij})}{kT}\right)$$

$$\left[\exp\left(- \frac{\Delta\ \varphi}{kT}\right) - 1\right] r_{12} r_{13} r_{23} dr_{12} dr_{13} dr_{23}. \qquad (17)$$

If it is assumed further that $\Delta\ \varphi$ is a small quantity, then

$$\Delta C(T) \approx \frac{8\pi^2 N^2}{3}\ \beta \int\int\int \Delta\ \varphi\ \exp\left(-\beta \sum_{i < j} \varphi\ (r_{ij})\right) r_{12} r_{13} r_{23} dr_{12} dr_{13} dr_{23} \qquad (18)$$

In this linear approximation, the quantity $\Delta C(T)$ is decoupled as

$$\Delta C = \Delta C_{rep} + \Delta C_{att} \qquad (19)$$

where $\Delta C_{rep(att)}$ is a function of the assumed pair potential, the temperature, and $\Delta\ \varphi_{rep} \left(\Delta\ \varphi_{att}\right)$.

Sherwood (10, 11) in effect rewrote equations 17-19 in terms of reduced units as

$$C^*(T^*) = C^*_{add}(T^*) + \Delta C^*_{att}(T^*) + \Delta C^*_{rep}(T^*) \qquad (20)$$

where $C^* = \frac{C}{b_o^2}$ and b_o is the covolume, which is equal to $\frac{2}{3}\ \pi\ N\ \sigma^3$.

He introduced the reduced units $r^* = \frac{r}{r_m}$, $T^* = \frac{kT}{\epsilon}$, $\varphi^* = \frac{\varphi}{\epsilon}$, $\alpha^* = \frac{\alpha}{\sigma^3}$, $\epsilon^* = \frac{\epsilon\ \sigma}{e^2}$ and changed the integration pattern by the transformation $r^*_{12} = xr^*$, $r^*_{13} = yr^*$, $r^*_{23} = r^*$ to obtain

$$C^*_{add} = - 36 \left(\frac{r_m}{\sigma}\right)^6 \int_0^\infty \int_{\frac{1}{2}}^1 \int_{1 - y}^y f(r^*) f(yr^*) f(xr^*) xyr^{*5} dxdydr^* \qquad (21)$$

where $f(s) = \exp(-\varphi^*(s)/T^*) - 1$,

$$\frac{\Delta C^*_{att}}{\alpha^*} = -\frac{27}{T^*}\left(\frac{r_m}{\sigma}\right)^3 \int_0^\infty \int_{\frac{1}{2}}^1 \int_{1-y}^y \exp\left(-\frac{\sum \varphi^*(r^*_{ij})}{T^*}\right) \frac{\sum \varphi^*_{att}(r^*_{ij})}{\sum r^{*\,-6}_{ij}}$$

$$(xy)^{-2} r^{*\,-4} \left[1 + 3\cos\theta_1 \cos\theta_2 \cos\theta_3\right] dxdydr^* \qquad (22)$$

$$\frac{\Delta C^*_{rep}}{\sqrt{\epsilon^*}} = -72\left(\frac{r_m}{\sigma}\right)^{\frac{13}{2}} \frac{1}{T^*}\int_0^\infty \int_{\frac{1}{2}}^1 \int_{1-y}^y \exp\left(-\frac{\sum \varphi^*(r^*_{ij})}{T^*}\right)\left(\varphi^*_{rep}(r^*_{12})\varphi^*_{rep}(r^*_{13})\varphi^*_{rep}(r^*_{23})\right)^{1/2}$$

$$(xy)^{\frac{3}{2}} r^{*\frac{11}{2}} \left[d^{-1}_{1(23)} + d^{-1}_{2(13)} + d^{-1}_{3(12)} - x^{-1} - y^{-1} - 1\right] dxdydr^* \qquad (23)$$

where

$$d_{1(23)} = \frac{1}{\sqrt{2}}\sqrt{x^2 + y^2 - \frac{1}{2}}$$

$$d_{2(13)} = \frac{1}{\sqrt{2}}\sqrt{x^2 + 1 - \frac{1}{2}y^2}$$

$$d_{3(12)} = \frac{1}{\sqrt{2}}\sqrt{y^2 + 1 - \frac{1}{2}x^2}$$

The point $x = \frac{1}{2}$ poses mathematical difficulties in computing ΔC_{rep}. Sherwood and coworkers (10) avoid this region by noting that the asymptotic expansion of the Gaussian model, equation (5-a), fails for any angle greater than 100°, and that the full Gaussian model is near zero in this region. Hence, the integrand was set equal to zero for $d_{1(23)} \leq 0.4196$.

The temperature range for the above expressions is valid for $T \gg 75^\circ$ K, since for lower temperatures the thermal wavelength for helium is greater than the molecular diameter, and consequently quantum effects become important.

The quantities C^*_{add}, $\Delta C^*_{rep}/\sqrt{\epsilon^*}$, $\Delta C^*_{att}/\alpha^*$ were computed on an IBM 1620 computer[4] for $T^* = 10$, 20, 30, 40, and 100 using Simpson's rule for numerical integration. The programs prepared by ADP were HA 2983, HA 2860, and HA 3068, respectively. Table 2 gives the results of these calculations for $\Delta C^*_{rep}/\sqrt{\epsilon^*}$, corresponding to three cutoff angles considered: 90°, 100°, and 110°. The only parameter specified was γ, and Mason and Rice's (6) value of 12.4 was used.

TABLE 2. - Computer results for C^*_{add}, $\Delta C^*_{rep}/\sqrt{\epsilon^*}$, and $\Delta C^*_{att}/\alpha^*$ for five reduced temperatures

	$\Delta C^*_{rep}/\sqrt{\epsilon^*}$				
T^*	$\theta < 90^\circ$	$\theta < 100^\circ$	$\theta < 110^\circ$	$\Delta C^*_{att}/\alpha^*$	C^*_{add}
10	-0.27834072	-0.31529681	-0.33905768	0.65578836	0.24980667
20	-.22286077	-.25651750	-.27904013	.35936268	.19817531
30	-.20501932	-.23823513	-.26098726	.25997038	.16647585
40	-.19590474	-.22921635	-.25241581	.20870606	.14468615
100	-.17734976	-.21233969	-.23804442	.10876412	.084953389

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[4] Reference to specific models of equipment is made for identification only and does not imply endorsement by the Bureau of Mines.

COMPUTATIONS OF C^*_{add}

The integration scheme for C^*_{add} was $\Delta r^* = .0125$ for $0 < r^* < 3$ and $\Delta r^* = .025$ for $3 < r^* < 6$ and $\Delta Y = \Delta X = .0125$ for $0 < r^* < 6$. This is a refinement over the interval size selected by Sherwood and Prausnitz (11). The error involved in using Simpson's rule is estimated to be within 1 percent by comparison of results for successive interval sizes. The discontinuities which occur in the integrand whenever r^*, xr^*, or yr^* equals m^* were accounted for by applying Simpson's rule only to continuous regions, avoiding integration over discontinuities. The computer program would adjust for the discontinuities by selecting the next smallest subinterval size for the integration according to the first larger even number of subintervals which would produce a subinterval smaller than (or equal to) the specified subinterval size. It seems to this author that this was not considered by Sherwood and Prausnitz (11) for the following reason. Their value of 0.2798 for C^*_{add} for $\gamma = 15$ and $T^* = 10$ was reproduced using their subdivision scheme. A result of 0.2837 was obtained by using the same subinterval size, but accounting for the discontinuities. This seems to be a significant computational improvement. This aspect was incorporated into the computations of ΔC_{rep} and ΔC_{att} also.

COMPUTATIONS OF $\Delta C^*_{rep}/\sqrt{\epsilon^*}$

The integration pattern selected for $\Delta C^*_{rep}/\sqrt{\epsilon^*}$ was $\Delta r^* = .02$ for $0 < r^* < 2.5986383$ and $\Delta Y = \Delta X = .015625$. As mentioned above, discontinuities were accounted for in the integration. The results

are larger in absolute value than those found by Sherwood and coworkers (10) for the LJ (12, 6) potential. It is seen from table 2 that a change in cutoff angle from 100° to 90° or 110° produces changes in $\Delta C^*_{rep}/\sqrt{\epsilon^*}$ from 7.5 percent to 16.5 percent, where the discrepancy increases with increasing temperature. However, the Gaussian model itself is subject to criticism, as noted by Sherwood and coworkers (10). The net effect of the contribution of $\Delta C^*_{rep}/\sqrt{\epsilon^*}$ is to lower the third virial coefficient. The same procedure was used to select the best interval size as above, which is within an error of 0.4 percent.

COMPUTATIONS OF $\Delta C^*_{att}/\alpha^*$

The integration pattern for $\Delta C^*_{att}/\alpha^*$ was $\Delta r^* = .01$ for $0 < r^* < 2$, $\Delta r^* = .02$ for $2 < r^* < 10$, and $\Delta Y = \Delta X = .015625$. The subinterval length was one-half that used by Sherwood and Prausnitz (11). The effect of discontinuities were accounted for as before. The net effect of this correction to the third virial is to raise the curve. The error in the subinterval size used involves no error greater than five one-thousands of 1 percent.

In all cases the cutoff error in the r* integration was estimated to be within one-tenth of 1 percent.

COMPARISON OF C^*_{add}, ΔC^*_{rep}, and ΔC^*_{att}

Table 3 lists hand calculator results applied to table 2 for specified values of ε and α for helium, and the quantity ΔC^*_{rep} is listed for Mason and Rice's (6) value of ε. ΔC^*_{att} is listed for two extreme cases of α: one is the value in the literature by

Kihara (4), and the other is the theoretical value calculated by Slater and Kirkwood (12). It is felt that the actual value should lie somewhere in between the two extremes. The results of table 3 show that the contribution ΔC increases with α.

The quantities ΔC^*_{rep} and ΔC^*_{att} are comparable in magnitude but of opposite sign, which, as reported earlier (10, 11) yields a small net contribution. In table 4 it is seen that $|\Delta C|$ is less than 2 percent of $|C_{add}|$.

TABLE 3. - ΔC^*_{att} for $\alpha = .201$ Å^3 and $\alpha = .210$ Å^3, ΔC^*_{rep} for $\epsilon/K = 9.16°$ K, and ΔC^*

	ΔC^*_{att}		ΔC^*_{rep}	ΔC^*	
T, °K	$\alpha = .201$ Å^3[1]	$\alpha = .210$ Å^3[2]	$\theta < 100°$	$\alpha = .201$ Å^3[1]	$\alpha = .210$ Å^3[2]
91.6	0.006296	0.006558	-0.003878	0.002418	0.002680
183.2	.003450	.003594	-.003155	.000295	.000439
274.8	.002496	.002600	-.002930	-.000434	-.000330
366.4	.002004	.002087	-.002819	-.000815	-.000732
916	.001044	.001088	-.002612	-.0001568	-.001524

[1] Kihara (4).
[2] Slater and Kirkwood (12).

TABLE 4. - Percent ratio of $|\Delta C|$ to $|C_{add}|$

	$\left\|\frac{\Delta C}{C_{add}}\right\|$ percent[1]	
T, °K	$\alpha = .201$ Å^3[2]	$\alpha = .210$ Å^3[2]
91.6	0.97	1.07
183.2	.15	.22
274.8	.26	.20
366.4	.56	.51
916	1.845	1.79

[1] Calculated from tables 2 and 3.
[2] See footnotes to table 3.

DISTRIBUTION FUNCTIONS FOR ΔC^*, ΔC^*_{rep}, and ΔC^*_{att}

The quantities ΔC^*_{rep} and ΔC^*_{att} can be written as

$$\Delta C^*_{rep} = \sqrt{\epsilon^*}\, N \int\int\int f(x,y,r^*)\, dxdydr^* \tag{24-a}$$

$$\Delta C^*_{att} = \alpha^*\, M \int\int\int g(x,y,r^*)\, dxdydr^* \tag{24-b}$$

where N and M are constants

and

$$\Delta C^* = \Delta C^*_{att} + \Delta C^*_{rep} \tag{24-c}$$

The normalized distribution functions which have been averaged over all configurations for some given separation r* of two of the three atoms are

$$C^*_{rep}(r^*) = \frac{N}{|N|}\, \frac{\int\int f(x,y,r^*)\, dxdy}{\left|\int\int\int f(x,y,r^*)\, dxdydr^*\right|} \tag{25-a}$$

$$C_{att}(r^*) = \frac{M}{|M|}\, \frac{\int\int g(x,y,r^*)\, dxdy}{\left|\int\int\int g(x,y,r^*)\, dxdydr^*\right|} \tag{25-b}$$

$$C^*(r^*) = \frac{|\Delta C^*_{rep}|}{|\Delta C^*|}\, C^*_{rep}(r^*) + \frac{|\Delta C^*_{att}|}{|\Delta C^*|}\, C^*_{att}(r^*) \tag{25-c}$$

The values of C^*_{rep}, C^*_{att}, and C* as given by equations 25-a, 25-b, and 25-c are plotted in figures 2 and 3 for α = .201 $\mathring{A}^3$ and Mason

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Figure 2. - Distribution Functions for ΔC^*, ΔC^*_{rep}, and ΔC^*_{att} at T* = 10.

Figure 3. - Distribution Functions for ΔC^*, ΔC^*_{rep}, and ΔC^*_{att} at T* = 100.

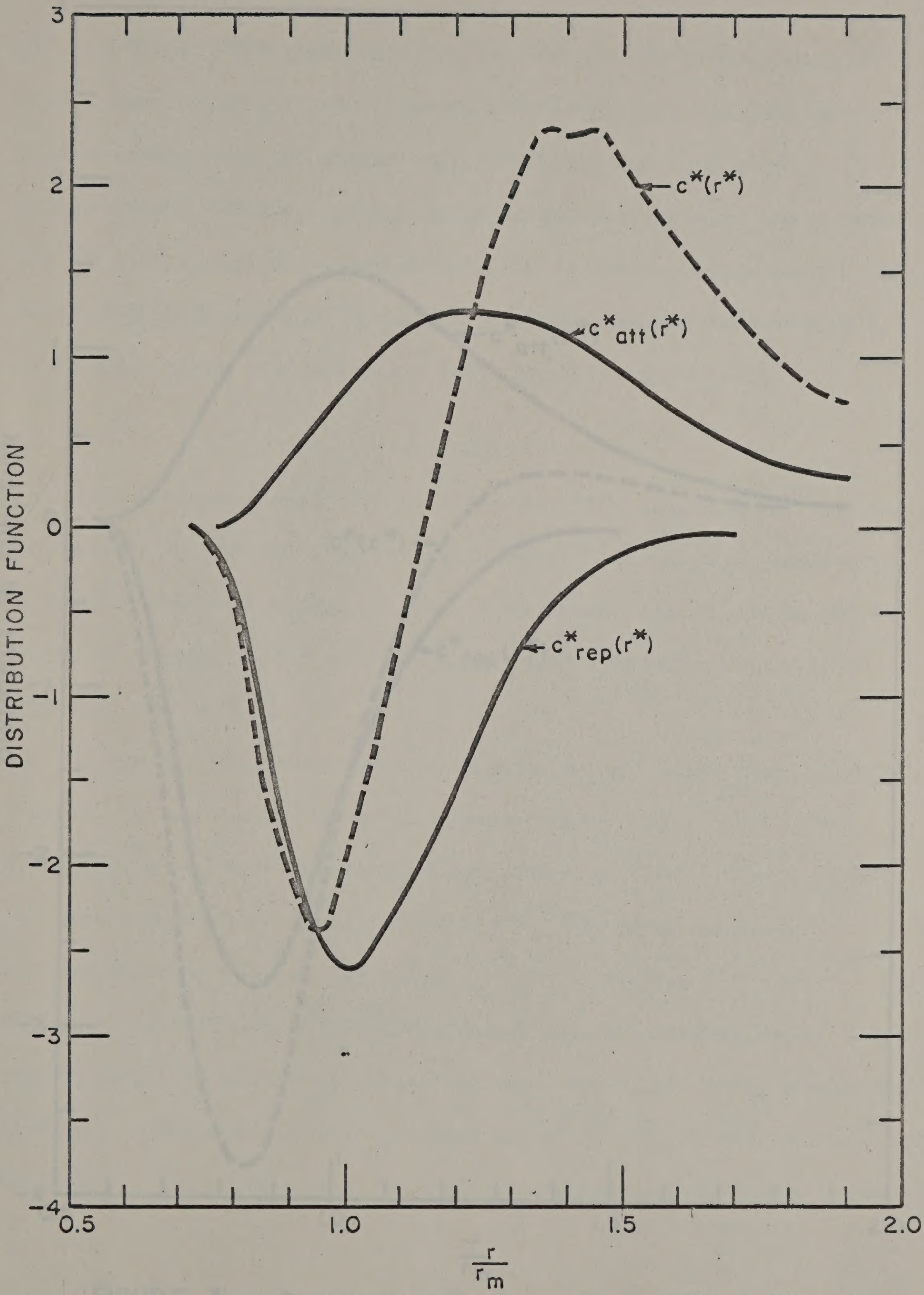

FIGURE 2. – Distribution Functions for ΔC^*, ΔC^*_{rep}, and ΔC^*_{att} at $T^* = 10$.

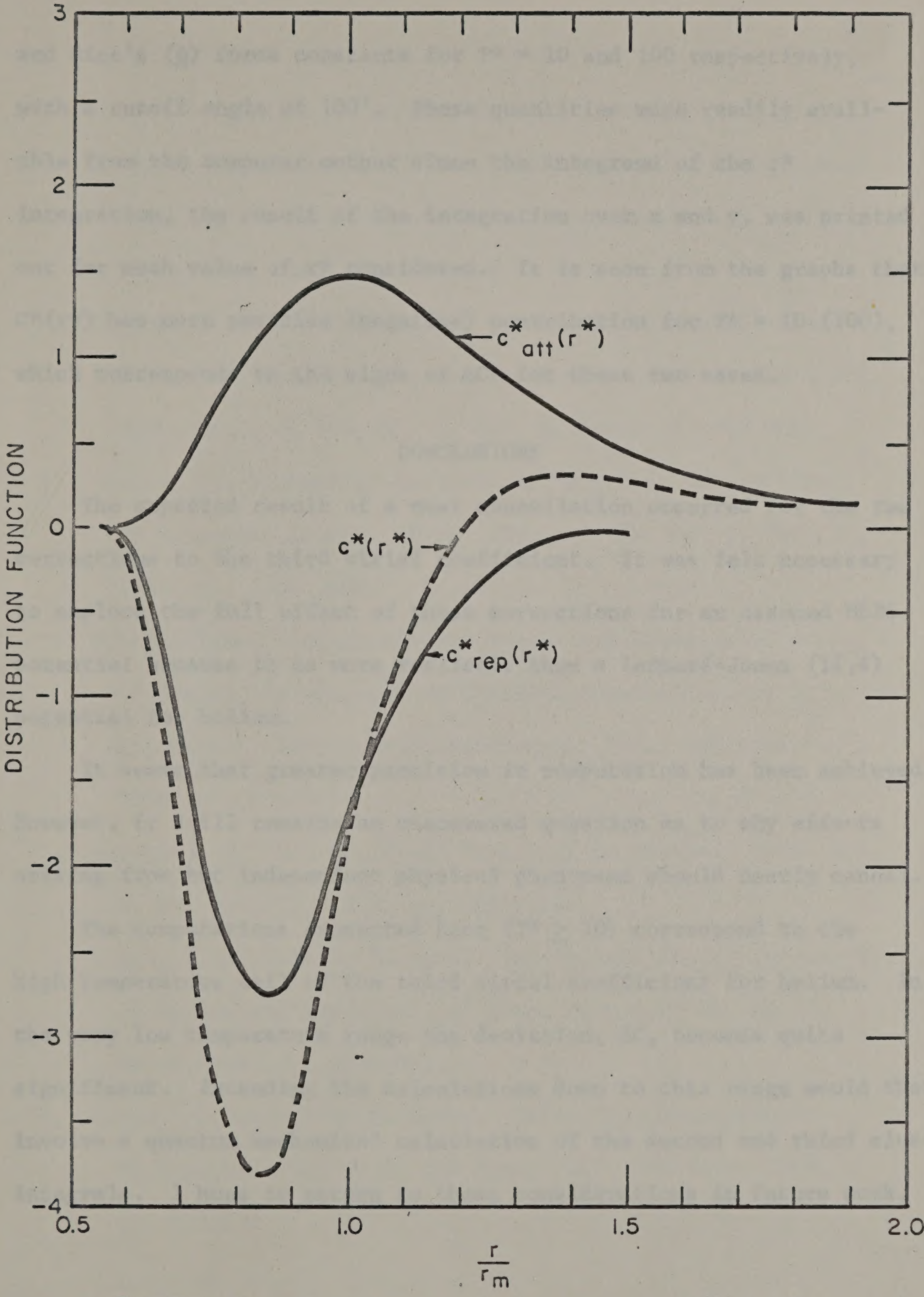

FIGURE 3. - Distribution Functions for ΔC^*, ΔC^*_{rep}, and ΔC^*_{att} at $T^* = 100$.

and Rice's (6) force constants for $T^* = 10$ and 100 respectively, with a cutoff angle of 100°. These quantities were readily available from the computer output since the integrand of the r^* integration, the result of the integration over x and y, was printed out for each value of r^* considered. It is seen from the graphs that $C^*(r^*)$ has more positive (negative) contribution for $T^* = 10$ (100), which corresponds to the signs of ΔC^* for these two cases.

CONCLUSIONS

The expected result of a near cancellation occurred for the two corrections to the third virial coefficient. It was felt necessary to explore the full effect of these corrections for an assumed MBE6 potential because it is more realistic than a Lennard-Jones (12,6) potential for helium.

It seems that greater precision in computation has been achieved. However, it still remains an unanswered question as to why effects arising from two independent physical phenomena should nearly cancel.

The computations presented here ($T^* \geq 10$) correspond to the high temperature tail of the third virial coefficient for helium. In the very low temperature range the deviation, ΔC, becomes quite significant. Extending the calculations down to this range would therefore involve a quantum mechanical calculation of the second and third cluster integrals. I hope to return to these considerations in future work.

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